



Magnetic solid-phase extraction based on graphene oxide for the determination of lignans in sesame oil



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ABSTRACT

Graphene oxide was fabricated by a simple method and applied to magnetic solid-phase extraction. In a pretreatment procedure before the sesamol, sesamin and sesamolins in sesame oil were detected by high performance liquid chromatography. Several parameters affecting the extraction efficiency were investigated, including the type and volume of desorption solvent, desorption time and the amount of sorbent. Under the optimized conditions, the detection limits of sesamol, sesamin, and sesamolins were 0.05 µg/g, 0.02 µg/g, and 0.02 µg/g, respectively. The limits of quantification were all 0.2 µg/g. The average recoveries of sesamol, sesamin, and sesamolins were 84.55%, 85.47%, 86.83%, respectively and their relative standard deviations were 1.23%, 1.33%, and 0.84%, respectively.

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1. Introduction

Sesame seeds were regarded as a healthy food containing lignans such as sesamol, sesamin and sesamolins, which improve the stability of sesame oil (Huang, Song, Sun, & Bao, 2011; Namiki, 1995; Zhang, Li, Wang, & Wang, 2005). Studies showed that the lignans in sesame oil had many physiological functions, such as alcohol metabolism promotion, lipid metabolism regulation, anti-cancer function, anti-mutation and liver protection (Hemalatha, Raghunath, & Ghafoorunissa, 2004; Kushihiro, Masaoka, Hageshita, Akahashi, & Sugano, 2002; Ren, Yuan, Ling, & Li, 2012). The contents and types of lignan in sesame oil are not only an important index for evaluating sesame oil quality, but also a basis for determining high quality sesame varieties.

To eliminate the influence of lipid components on oil samples in the process of detecting lignans in sesame oil, pretreatment of oil samples is a key step. Solid phase extraction (Chen et al., 2012; Li & Zeng, 2011), liquid-liquid extraction (Rangkadilok et al., 2010; Reshma et al., 2010), thin layer chromatography

(Kamal-Eldin, Yousif, & Appelqvist, 1991; Zhao, 2005), and saponification (Xue et al., 2006) are the main pretreatment methods. However, those methods have some disadvantages including high complexity, low sensitivity, and a long processing cycle. In recent years, magnetic solid phase extraction (MSPE) has received wide attention in the sample preparation field (He, Liu, Li, Zhou, & Wang, 2012; Mehdinia, Roohi, & Jabbari, 2011; Qin, Fang, & Luo, 2011; Wang, Huang, Yu, Wang, & Shen, 2013), as the sample treatment is simple with the magnetic extraction medium directly dispersed in the sample solution. It is especially suitable for samples containing suspended solids and biological samples (Huang, Ding, & Feng, 2012).

Graphene oxide is an important derivative of graphene with a similar structure, which is composed of carbon atoms in the single-atom layer of a sp² hybrid connection. The basic unit of graphene is the most stable structure of a hexatomic ring in organic materials (Dai, Shao, Ma, & Pei, 2010). In this study, few-layer graphene oxide and hydroxylated Fe₃O₄ were combined and after sesame oil was pretreated by MSPE in combination with the liquid chromatography (LC) technology, a detection method was established for sesamol, sesamin and sesamolins in sesame oil. This method is fast and simple and has a good application prospect in detection of main lignans in sesame oil.

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2. Experimental section

2.1. Instruments and reagents

Sesamol, sesamin and sesamolol were analyzed on Agilent 1200 high performance liquid chromatography (HPLC) system (Agilent Technologies, Santa Clara, CA) equipped with a diode array detector (DAD). Flake graphite of spectroscopically pure was obtained from Beijing DK Nano Technology Co., Ltd. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sodium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene glycol, ethylenediamine, sulfuric acid (98%), potassium permanganate, dimethyl sulfoxide, dichloromethane, ethanol, acetonitrile, methanol, and hydrogen peroxide were obtained from Sinopharm Chemical Reagent Co., Ltd. Sesamol (purity 99%) was supplied by Nanjing Ze Lang Pharmaceutical Technology Co., Ltd. Sesamin and sesamolol spiked substances (99% purity) were obtained from China standard material network. All solvents used were of HPLC grade, unless otherwise specified. Sesame oil samples were purchased from local markets in Wuhan (China).

2.2. Methods

2.2.1. Preparation of hydroxylated Fe_3O_4 magnetite nanoparticles (MNPs)

Monodisperse Fe_3O_4 MNPs with mesoporous structure were synthesized via a solvothermal process according to a previously reported method (Wei et al., 2013). In Brief, after 5 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was completely dissolved in 100 mL ethylene glycol, 15 g sodium acetate and 50 mL of ethylenediamine were added and vortex stirred for 30 min before reaction in a Teflon-lined stainless steel autoclave (200 mL) for 8 h under 200 °C. The product was washed with 50 mL of water/ethanol (1:1, v/v) five times and vacuum-dried at 60 °C for 6 h.

2.2.2. Preparation of graphene oxide

The synthesis of graphene oxide was performed using KMnO_4 and a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ as oxidizing agents according to the method reported by Marcano and co-workers (Marcano et al., 2010). Briefly, 3.0 g of flake graphite was added to 400 mL of mixture of sulfuric acid and phosphoric acid (volume ratio 9:1). After stirring for 10 min, 18.0 g of potassium permanganate was added into the mixture. Potassium permanganate was added slowly in case of the reaction temperature exceeded 20 °C. Then the mixture was heated to 50 °C and stirred for 12 h. After the reaction was completed, the mixture was cooled to room temperature, and 400 mL of ice water was poured in and stirred continuously for half an hour. Then, 30% hydrogen peroxide was added dropwise into the reaction system until the solution turned into bright yellow. The mixture was kept overnight and then the supernatant was discarded. The solution was washed with 1 L 5–10% hydrochloric acid three times and with 1 L of deionized water five times so as to remove metal ions, sulfate and chloride ions. Finally, the solid was freezing dried and then placed in deionized water for preparation of 1 mg/mL water solution. Later it was ultrasonic for 1 h. When oxidized graphene was dissociated into graphene oxide, the solution was centrifuged for 30 min at 1000 rpm and then the supernatant was removed. The sediment was then dried at 50 °C and the graphene oxide powder was obtained.

2.2.3. Synthesis of magnetic graphene oxide

The synthesis of magnetic graphene oxide was performed according to the method reported by Ding et al. (2011) and Luo, Shi, Gao, and Feng (2011). After 0.1 g of hydroxylation Fe_3O_4 MNPs and 0.04 g of graphene oxide were mixed by 40 mL of dimethyl

sulfoxide, the mixture was ultrasonic treated in a water bath for 30 min at room temperature. Then, materials were obtained and the enrichment concentrations became 3.5 mg/mL.

2.2.4. Sample extraction process

2.2.4.1. Magnetic solid-phase extraction. Sesame oil of 0.1 g was added into a test tube (10 mL), in which 4 mL dichloromethane was mixed, vortexed and dissolved. Then, 1.4 mg magnetic graphene oxide was added and vortexed intensively for 3 min. Sesamol, sesamin and sesamolol were adsorbed onto the surface of magnetic graphene oxide. And then an external magnetic field was applied at the bottom of the tube to gather adsorption agents before the supernatant was discarded. After cleanup by 1 mL dichloromethane solution, the supernatant was removed by the magnetic field. Later, 1.7 mL methanol was added into the remaining precipitate and vortex-shaken for 1.5 min for desorption. They were then separated by the external magnetic field, and the supernatant was collected for HPLC analysis.

2.2.4.2. Saponification method. The saponification method in previous literatures were used (Xue et al., 2006). The oil was extracted from the prepared sesame seeds with hexanes for 4–5 h in a Soxhlet apparatus. The organic solvent was removed from the extract under vacuum using a water bath. Sodium hydroxide (1 g) dissolved in distilled water (5 mL) and pure ethanol (10 mL) were added into the oil sample (0.5 g). The mixture was stirred for 30 min at 80 °C and then extracted trice by petroleum ether (100 mL). The solvent was removed from emerged extracts under vacuum using rotary evaporation. Finally, the concentrate was suspended in 50 mL of methanol.

2.2.4.3. Alumina column chromatography method. Alumina column chromatography was referred to previously published literature (Liu, Wang, & Jin, 2004). Alumina used for chromatography was activated at the temperature of 190 °C. After the activated alumina was added into the column which contained a certain amount of petroleum ether, the column was washed twice by elution solution for column equilibrium. Sesame oil sample (5 g) dissolved by petroleum ether was applied to a chromatographic column packed with alumina and eluted first with 100 mL of petroleum ether, and then 150 mL of ethyl acetate. The eluate was collected and vacuum evaporated to remove the adsorbed solvent. Then it was diluted by 50 mL of acetone for HPLC analysis.

2.2.5. Liquid chromatography conditions

Chromatographic separation was performed on a Kromasil C-18 column: (4.6 mm × 150 mm, 5 μm) with a methanol water (75:25, V/V) mobile phase at a flow rate of 0.8 mL/min and the injection volume was 20 μL. UV detection wavelength was 290 nm.

3. Results and discussion

3.1. Optimization of extraction conditions

3.1.1. Types of desorption solvents

Different amounts of sesamol, sesame and sesamolol standards were added into sesame oil of known contents, each gram of which contained 0.030 mg of sesamol, 0.025 mg of sesamin and 0.030 mg of sesamolol. According to the sample extraction method described in Section 2.2.4, the sesamol, sesamin and sesamolol recoveries were respectively determined when the desorption solvents were pure methanol, acetonitrile and ethanol. Each level of extraction condition was measured 4 times and their average were separately obtained. The calculation formula was as follows:

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